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Evaluation of a FTIR (Fourier Transform Infrared Spectrometer) Mobile Source Measurement System

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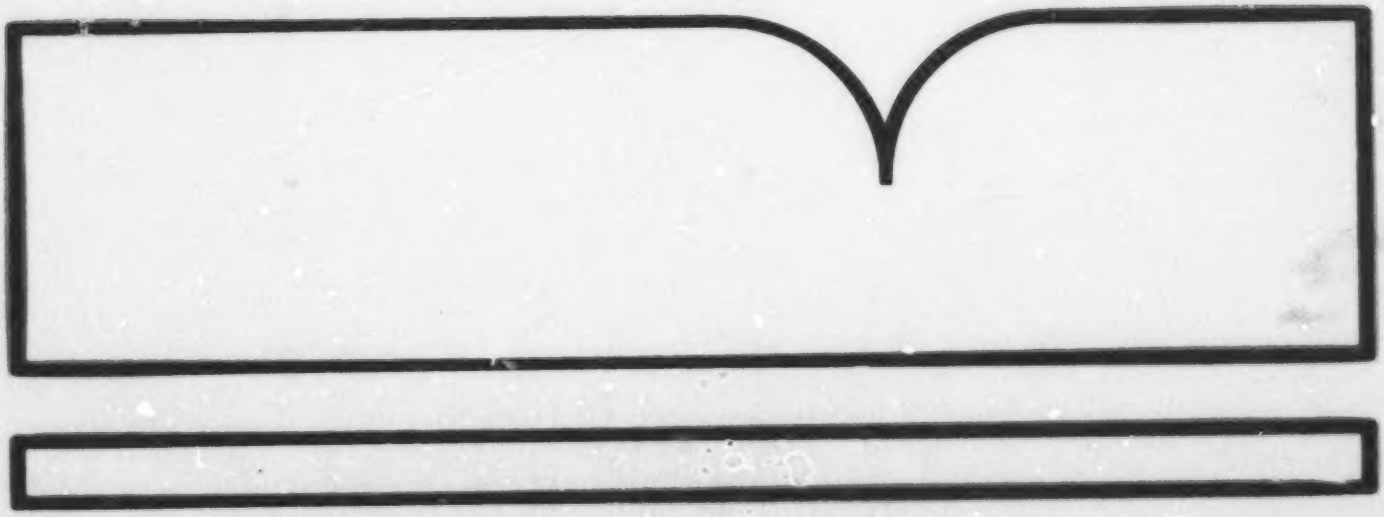

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EVALUATION OF A FTIR MOBILE SOURCE MEASUREMENT SYSTEM

A Status Report

by

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SECTION 1

INTRODUCTION

Mobile Sources emissions are major contributors to air pollution and in particular to the "California" smog. Early measurements of these emissions where made by "wet" chemical methods but as the number of the measurements increased so did the effort to make the measurements instrumental. The primary technique was non-dispersive infrared absorption spectroscopy. The degree to which the technique could be applied was limited by the nature of the measurements to be made and some of the basic limitations of the infrared technique. This approach is still the method of choice for the measurement of carbon dioxide and carbon monoxide.

Tailpipe emissions from spark ignited engines were the initial concern. These emissions result from the incomplete combustion reaction of gasoline with air.

$$\underset{\text{Gasoline}}{[CH_2]_n} + \underbrace{11/2O_2 + 6\ N_2}_{\text{Air}} = H_2O + CO_2 + 6\ N_2$$

The reaction shown is a simplified stoichiometric reaction. The reaction produces about 15 % each of carbon dioxide and water. To the extent that the reaction is incomplete, carbon monoxide is substituted for carbon dioxide as are the hydrocarbons, both unburned and reaction products.

Aldehydes, primarily formaldehyde, are among the reaction products. As long as the fuel used was gasoline it was observed that the relative proportion of aldehydes to gasoline hydrocarbons was relatively consistent and that all techniques used to reduce hydrocarbon emissions also reduced the aldehyde emissions, often preferentially. This made the specific measurement of the aldehydes unnecessary, except to the extent required to show that the situation had not changed. Concentrations of specific emissions, such as the aldehydes, individual hydrocarbons, and a variety of other pollutants, both organic and inorganic, are in the range of parts per billion to parts per million.

The emissions are diluted to a constant volume, to prevent the condensation of water, to slow some very fast chemical reactions, and to integrate the emissions over time. When a vehicle is operated over a reasonable driving cycle, significant changes in the emission of individual pollutants occur in less than 1 s. However, if measurements are made at a rate much higher than 10/s, one begins to see the effects of the firing of individual cylinders, which has little value from an overall emissions point of view. If measurements are made much less often than 1/s the transient excursions of individual pollutants such as nitric oxide begin to be lost. Therefore, the measurement of real-time emissions on the basis of one measurement per second is generally accepted for the definition of the real-time emission patterns of a vehicle.

For the determination of mass emission factors and gross emission patterns, integrated measurements are made which may be from bags collected over a whole cycle or part of one, or from the integration of the real-time emissions. Integrated emissions should agree whether the integration was physical, as in the bag analysis, or mathematical, as in the case of real-time emissions.

The problem of specificity in measuring parts per million concentrations of individual species in the presence of percent quantities of water and carbon dioxide was often insurmountable using infrared spectroscopy. The infrared systems were also limited by their inability to detect a concentration of less than about a part per million in an acceptable path length (less than about 40 m). In cases such as formaldehyde, emissions at sub PPM levels may account for 20 to 50 % of the total emissions.

The advent of Fourier transform infrared (FTIR) spectroscopy and improvements in detector sensitivity with reductions in noise levels due to solid state electronics have recently lowered the limits of detection. FTIR allows high-resolution scans to be made in acceptably short time frames. The resolution is great enough to allow a wide variety of compounds to be measured by looking "between" the water and CO2 bands, which previously obscured the other compounds.

In 1979 Maker et al of Ford Motor Company (1) described the application of FTIR spectroscopy to the analysis of automotive emissions. They also described a technique of data analysis in which they "subtracted" a matrix of components to determine the composition of the exhaust. This application of multiple wavelength analysis for each component allowed for more sensitive and specific detection. However, there was some loss in the allowable dynamic range, which necessitates the utilization of multiple mask sets for components that vary over a wide range of concentration. The precision with which the analysis is made is determined by the upper value of the mask, and thus the lowest possible range should be used which encompasses the data. If the data exceeds the value of the mask, indeterminate negative data is output. If the raw data is saved, it may be analyzed by more than one mask set.

The technique was further defined by the Ford group in the 1980s (2,3). Also during this time the application of FTIR in a more classical fashion was demonstrated by a consortium from VW and from Nicolet (4-7).

The original Ford work was conducted on an instrument constructed at that company. Latter work was done on a commercial FTIR instrument, but the software used was that developed by Ford for this specific application. This software is extensive and very specific. The VW/Nicolet group used commercially available spectrometers and applied more standard techniques to the data analysis but the data processing software is still unique to the application, as is the basic sampling methodology. Ford has since licensed Mattson Instruments Corp. to sell its software and methodology in conjunction with the Mattson Instruments' FTIR. This application appears to be becoming viable as a general Mobile Source analytical technique.

This technique has been successfully utilized, by Ford, to measure a wide variety of compounds including the regulated emissions, formaldehyde and

methanol. The raw data may be stored and analyzed latter for compounds not sought initially.

Since the FTIR technique is useful for the simultaneous measurement of almost all the pollutants of interest, the EPA Office of Mobile Sources, Ann Arbor, (OMS) became very interested in its application to production testing and to the analysis of formaldehyde and methanol. These latter analyses require individual sample collection with chromatographic analysis and are very manpower intensive. The importance of these analyses has been greatly intensified by the developing interest in the use of alcohols as alternate fuels.

Ford Motor Co. has also expressed a desire to use data obtained in this fashion for compliance and other testing. If this data is to be accepted, equivalency must be shown.

OMS assigned this work its highest priority, Category #1 - Critical. This priority was carried forward until funds became available to implement the program in fiscal year 1986. In July 1986 EPA authorized NSI to (1) prepare a detailed evaluation of the current state of the art in analysis of mobile source emissions with special emphasis on FTIR and (2) recommend acquisition of the best available unit. The initial evaluation was not limited to FTIR because historically several other techniques such as mass spectroscopy had shown potential in being able to fulfill the needs of this application. It was desired to determine the best method(s) to use in production and research situations.

This evaluation included visits to Ford, Nicolet, and the NY Department of Environmental Protection, which was operating an FTIR unit. The final evaluation was prepared in April 1987 and recommended that an FTIR be obtained from either Mattson Instruments or Nicolet on the basis of specifications required for mobile source analysis. The system was to include all hardware and software required for operation. Open bids were requested by NSI. There were only two responses, Nicolet and Mattson Instruments, with Mattson Instruments the low bidder. The specifications listed in the justification are shown in Appendix A. Initial delivery of hardware occurred in March 1988.

SECTION 2

CONCLUSIONS

The system appears to have a large potential for utilization in both routine emissions measurements, where it could replace several instruments currently used, and in research evaluations of fuels and vehicle emissions. The ability to adapt the basic routine instrument to analyze additional compounds that might be required due to changes in technology is very attractive. This would require only a change in the mask set utilized. No change or addition of instrumentation would be required. This potential must be further explored.

The research potential of the system is large. The emission rate of individual components may be followed and evaluated. This capability requires only that they have a reasonably intense and specific infrared spectra.

The system evaluated is a prototype system that is still incomplete. It is now apparent that a larger hard drive and a larger mass storage system are necessary for the archival storage of the spectra for future evaluation.

Hardware reliability is a major issue. The system rarely operates for more than a few weeks at a time without the necessity of service. The problems which appear to be in the spectrometer are inexplicable because the basic hardware is the same as that in the top of line version of the Mattson Instruments commercial system. According to Mattson differences between our system and the commercial system are in the computer and its peripherals.

Software deficiencies fall into several categories and each have their own priority.

Software reliability must be improved to a point where the system will operate properly when started.

The software is not currently user friendly. The software should be made simpler to use for routine application by non-spectroscopists.

It is highly desirable that the system be operable in the multi-user mode.

It is also desirable that data display and processing be allowed during data acquisition.

The ability to create, edit, and modify masks is a requirement for a working system. This ability is currently available only through the kindness of the Ford Motor Co. and the use of their initial system.

The system has no graphics capability. It would be desirable to be able to plot spectra on the screen and to manipulate these spectra. Currently, spectra are created, stored, translated and can then be transmitted for external hard-copy plotting. Spectral subtraction is the only function available for spectral manipulation. This function is extremely awkward and time- consuming to use

because of the external plotting requirement, which requires that, for each subtractive iteration, the resultant spectra be created, translated, transferred and a hard copy plot created. Baseline correction and smoothing are examples of common spectral tasks that can not be preformed. Such functions are highly desirable if optimal utilization is to be made of the unit.

The default mask set should be changeable. With its current default mask set, the system comes up ready to test cars operating on ethanol. This mask set must be changed each time the system is started.

Multiple masks are required for compounds which are present over a wide range of concentrations. The system can now use only one mask per run. If the concentration of an individual component varies over a wide range, reprocessing the data with multiple masks and selecting the "appropriate" data from each data set are required. An "automatic span" selection of the appropriate mask is highly desireable.

The system does not reprocess data automatically. If an FTP is to be reprocessed with a separate mask set, each scan must be recalled individually, more than 600 scans for the three bags of the Federal Test Procedure. This is not practical and should be changed before the system is finalized.

The restrictions to 512 scans and the 3 s per scan are inhibiting.

The current system is restricted to real-time analysis by the software available.

SECTION 3

RECOMMENDATIONS FOR FUTURE WORK

These recommendations assume that the appropriate software and hardware modifications to make this a practical working system will be made within a reasonable period of time. Because the effort is considerably larger than apparently had been envisioned by Mattson Instruments and Ford, a maximum effort to cooperate and encourage completion of this work should be continued.

The current evaluation is incomplete. As the software/hardware is updated each change must be evaluated for efficacy and reliability.

The currently available masks, that have not yet been evaluated, should be tested for noise level, limits of detection, and linear range.

The analog signal inputs recently incorporated into software must be checked and evaluated.

A "Mini-dilution System" is part of the total FTIR System. This Mini-dilution tunnel allows a more concentrated signal to be seen by the FTIR with a concurrent lowering of the limits of detection. This addition should be evaluated.

SECTION 4

EVALUATION

DESCRIPTION OF SYSTEM

The system utilizes a standard Mattson Instruments FTIR coupled with a Masscomp Computer. This computer is larger and different from than those normally supplied by Mattson Instruments because of the large memory and high speed central processing unit (CPU) needed for this application. The original Ford software was developed and run on a DEC PDP 11/40 and will not run on the Masscomp without translation and rewriting. Disruptions in the translation occurred when Masscomp upgraded the version of the UNIX operating system that it was implementing on this computer between the time the order was placed and the time when it was delivered. The older software was not upwardly compatible. This occured at least twice.

Evaluation Criteria

The evaluation of this system covers three separate but allied areas. The use of infrared absorption spectroscopy or the derivative FTIR technology is not in question. This technique is known to be applicable but subject to limitations. It is the methodology by which these limitations are minimized that must be demonstrated. The FTIR system was directly connected to the CVS system as described by Ford. The three areas of evaluation are:

I. Precision and Accuracy of Batch Analysis
   - A. formaldehyde and methanol
   - B. Regulated Emissions, (except Total Hydrocarbon)
   - C. Analysis of other non-regulated compounds

II. Precision and accuracy of real-time analysis
   - A. Integrated values for comparison with batch analysis for groups 1.A and 1.B above.
   - B. Point by point comparison of regulated emissions
   - C. Application to the real-time analysis of other compounds. (not quantitative)
   - D. Application of the "mini-dilution" tunnel to increase sensitivity.

III. Basic instrument reliability and function as currently configured

These three primary areas are not additive. Each defines a separate facet of the techniques utility. Because of time constraints we have not been able to

investigate Part II.D at all, although the equipment is available.

This is a status report and as such represents only the current conditions in time and it is not a final evaluation of this technique or its implementation. This work will continue, at least for the immediate future, in hopes that the short comings will be resolved.

SECTION 5

RESULTS

PRECISION AND ACCURACY OF BATCH ANALYSIS

Formaldehyde and Methanol

Comparisons where made of the Mattson Instruments FTIR Real-time Emissions Analyzer System, called hereafter FTIR, with a variety of other analytical systems. Initially the system was calibrated with pure components in order to verify operation. As expected the system was sensitive to the pressure in the sample cell. Figure 1 shows a linear plot of pressure versus response for methanol. The regression coefficient of 0.98 is reassuring.

To check the FTIR for its methanol calibration, methanol was injected into the CVS tunnel at a constant rate. From this known rate of injection, the concentration of methanol present in the tunnel was calculated. Samples from the tunnel were also collected through bubblers for gas chromatographic (GC)analysis. The tunnel hydrocarbon concentration was also monitored by a Hot FID calibrated for methanol. Injections of methanol were made over background air and in the presence of auto exhaust. The FTIR measurement was useful for comparison only on the pure methanol injections.The amount injected was at least a factor of 3 higher than the amount present in the exhaust. The results of these experiments are shown in Table 1. The GC analysis and the hot FID gave reproducible and consistent results that were in agreement with amounts injected. There was one apparent outlier, 2.376, which was more than two standard deviations from the mean. This value was also an outlier for the GC analysis, indicating a possible injection problem. When that value is removed the FTIR/FID average drops to 1.35 and the relative standard deviation drops from 27 % to 15 %. Direct comparison of the FTIR and GC results yield the same conclusions.

Similar experiments were performed with formaldehyde. In this case, fresh formalin solution was injected into the tunnel. The results were compared with samples collected concurrently on DNPH-coated silica gel cartridges (8). These results are shown in Table 2. Both analytical methods had averages below 1 but the scatter of the data overlapped it. The ratios of the calculated amounts injected with the amounts analyzed had no statistical outliers. The standard deviations of both methods were in the 15 to 20 % range. Ratios were determined for the two techniques and the result was near unity but with one outlier and another point close. Seven of seventeen ratios exceeded 1.0. The two methods are in agreement.

Regulated Emissions

Similar tests were made with the regulated gaseous emissions. The results for carbon dioxide, carbon monoxide, propane and the oxides of nitrogen were very

linear, Table 3.

More interesting is a comparison of direct readings on collected CVS bags and the summations of the FTIR analysis. A Ford Escort that had been built by the manufacturer to operate on methanol blends was operated over the Federal Test Procedure (9,10). The collected CVS bags were analyzed by the regular CVS analytical bench. The CVS analytical bench is calibrated daily with certified commercial span gases and monthly with National Institute of Standards & Technology (NIST/NBS) gas mixtures.

Three emissions, carbon dioxide, carbon monoxide, and nitric oxide, are measured from the CVS bags. Formaldehyde is collected on cartridges which are directly connected to the CVS tunnel through a heated probe and analysed later. Methanol is measured by collection in a water filled bubbler directly connected to the CVS tunnel. Separate samples of formaldehyde and methanol are collected for each bag.

Fifteen runs were made in an effort to evaluate the FTIR. The results are shown in Tables 4 through 8. These runs fell into four separate series. On the first five runs the FTIR results were consistently higher than those from other methods, except for the carbon monoxide data. This was attributed to an erroneously high sample cell pressure caused by too small a line between the cell and gauge.

This situation was corrected and three more runs were made that showed good agreement for carbon dioxide, nitric oxides, and formaldehyde. Carbon monoxide was about 10% low and methanol about 35% high. The low carbon monoxide is attributed to the fact that the most desirable mask, of the three available, could not be used because of an error in its construction. The high methanol values are similarly attributed to mask deficiencies. Currently the software cannot access or edit the masks. This means that new compounds may not be added to the set and that errors in the present set can not be corrected.

The next set of three runs were inexplicably low. The system did not appear to be operating properly. Mattson Instruments retuned and realigned the system, after which operation appeared to return to normal.

After the realignment, four more runs were made. All of the previous runs had been made with the vehicle operating on M-85, that is, 85 percent methanol 15 percent gasoline. These last four runs were made with pure methanol, M-100, as the fuel. The results for this data set were as expected; carbon dioxide, oxides of nitrogen, and formaldehyde were in reasonable agreement. Methanol was high and carbon monoxide continued to be somewhat low.

Analysis of Other Non-regulated Compounds

Because of time and resource limitations other compounds which the FTIR analysed were not directly compared with paralell analytical techniques. A discussion of the results obtained is presented in II., C..

PRECISION AND ACCURACY OF REAL-TIME ANALYSIS

This same analytical bench used for the bag analysis was operated in a real-time mode during these runs to provide data for a point-by-point comparison with the FTIR data. This data is collected one set per second for the full FTP, that is, all three bags and the intervening soak period. This data was compared both graphically and on a point-by-point basis with the FTIR data. This comparison was made by using Lotus 123 (Registered Trademark) spreadsheets. The CVS data was imported as numbers, and averaged over 3 s intervals. This yielded a data set that was comparable to the FTIR set which was then imported into it. The FTIR data was aligned approximately for Bag 1 and then for Bag 3 on import. Exact alignment was not attempted because the time response for the CVS bench depends on the orientation of the analyzers; that is, those further down stream respond later than those upstream. This was particularly noticeable for nitric oxides and the hot FID, the latter being directly connected to the tunnel.

POINT-BY-POINT COMPARISON OF REGULATED EMISSIONS

The best possible time alignment was attained by plotting the two signals and offsetting one or the other until the best visual match attainable was achieved. An exact match was not obtainable because the averaging had to occur before the signals could be compared. This meant that up to 1.5 s displacements could have occurred.

The aligned data tracked very well in general, showing all the same features. Examples of a Bag 1 nitric oxide and a Bag 1 carbon dioxide match are shown in figure 2 A & B, which reveal peaks and valleys that are not as pronounced in the FTIR data. This is due to the large, approximately 5 L, cell volume of the instrument and the relatively low flow rate through it. There is probably complete mixing in this cell rather than the plug flow noted by the other analyzers. Of greater importance is that the general features seen are the same and that the sum seen by both systems is the same. A larger pump has been ordered which may improve this performance.

In addition to the tests on the methanol Escort described previously, the system was also utilized on a "dual fuel" prototype vehicle capable of being operated on gasoline, methanol or any mixture of the two. The tests in this series were baseline tests using pure gasoline which provided an opportunity to examine a more diverse set of emissions. There was also one FTP and one Highway Fuel Economy Test on M-85.

Point by point comparisons of the regulated emissions were made by ratioing the individual FTIR and analytical bench data points. The results are shown in Table 9. These comparisons are very similar to the previously described data. The change in variability between runs can be seen as a difference in apparent noise level of the FTIR data when the plots of the data are examined.

In general the FTIR data tracked the bench analytical data very well, but problems were noted. Figures 3-5 are illustrative of the type of problems possible. Figure 3, a plot of the carbon dioxide emissions, is typical of data that exceeds the mask calibration values; that is, the data goes strongly negative. However, this occurred only at the start of the run, and according to

the bench data taken concurrently, later carbon dioxide emissions were higher. This would indicate that the concentration of carbon dioxide was not the cause of the negative swing. Except for the negative swing the two data sets track nicely. The FTIR signal shows considerably more scatter or noise.

Figure 4 shows examples of both positive and negative swings, where as Figure 5 is an example of exclusively positive surges. The FTIR concentration data in Figure 5 was reduced in value by half to keep the curves on the same apparent scale. If the initial peak is multiplied by two, that brief segment would be in reasonable agreement. Unfortunately the reason for these excursions is not apparent, nor is the day-to-day variation in the noise level. Success can not be predicted from run-to-run or day-to-day.

C. Application to the Real-time Analysis of Other Compounds

Some of the most positive aspects of the system are illustrated in the next figures. Figure 6 illustrates the emissions of carbon monoxide and nitrous oxide during collection of bags 1 and 2 of the FTP. Carbon monoxide is emitted from the very beginning of the cycle, decreasing from an initial peak as the vehicle warms up. After about 250 s a minimum level is attained and maintained for the rest of the test. Nitrous oxide on the other hand is not present initially and only appears in measurable quantities after about 75 s. Nitrous oxide also tails off and reaches a minimum level before the carbon monoxide does. These changes are undoubtedly related to catalyst warmup.

This is demonstrated in Figure 7 which shows a plot of Nitrous oxide and ammonia along with temperatures measured before the catalyst. The temperature was measured by a thermocouple which was connected to the bench real-time system. Time alignment is not as precise as it will be when the revised software is implemented, which allows the direct collection of six external signals. From this data it can be seen that nitrous oxide is formed while the catalyst is warming up, around 400 degrees before the catalyst, and ceases after the catalyst is in full operation. Ammonia is not formed until the catalyst is fully warmed up and is then continuously emitted.

Figure 8 shows the emissions of formaldehyde and methanol on this same run. This is a run of the dual fuel car operated on gasoline. Formaldehyde is emitted early and then is effectively reduced after the catalyst is operational. The noise level of this signal is acceptable being in the +/- 0.2-ppm range.

Methanol appears to be emitted in small amounts during the initial warmup, as evidenced by the data being all above zero in that period. Unfortunately the high noise level of this signal, greater than +/- 1 ppm, makes this conclusion tenuous. It is possible that this high noise level is a mask assignment problem. This idea is supported by the analytical error seen in the methanol runs.

A number of individual hydrocarbons were measured on several runs and the integrated results compared with the results obtained by GC analysis, Table 10. Methane, ethylene, and propylene results agreed well; the standard deviations were in the 20 %. Acetylene was lower on the FTIR than on the GC by about half, but the scatter was large and the values were low. Ethane and 1,3-butadiene were consistently higher on the FTIR. The values were low but the results were fairly consistent.

Other compounds sought but not found included nitrogen dioxide, nitrous acid, hydrogen cyanide and formic acid.

III. Basic Instrument Reliability and Function as Currently Configured

A summary of the instrument log is shown in appendix B. In the ten months since the instrument was received, in mid April 1988, there have been numerous hardware malfunctions. There have been eleven adjustments to the optical bench, eight adjustments including three replacements of the moving mirror bearings, nine detector adjustments, and several other hardware problems.

There are problems related to the signal intensity. When the signal falls below the optimum level of about 30,000 (arbitrary units), response falls off. This behavior is inexplicable and is not typical of normal spectroscopic behavior. The response presented is a ratio of the unabsorbed signal to the absorbed signal. Both signals should change as the intensity changes. The signal intensity may be returned to the optimum value by opening the iris. This is done prior to runs for data. The value shown in the signal column are for a constant iris setting. When the system is realigned or otherwise serviced or repaired, the signal intensity usually returns to normal. The falloff begins again and is severe after a few weeks.

When the instrument was received the software was very incomplete and only short static runs could be made. At the end of September 1988 the software was upgraded to allow real-time data collection, and our evaluation began in ernest. Since that time several additions have been made to the software and numerous manufacturors service visits to "fix" the hardware have occurred. Interaction among EPA, NSI, Ford, and Mattson Instruments has been frequent and rewarding. Because the software is proprietary and original, there is little documentation at this time. As a result, the telephone and personal visits have been major, valuable resources. The ability to discuss problems and results with others who are doing similar work has been invaluable.

The FTIR will not operate in the multi-user mode of the operating system. When the real-time software is addressed from that version, the system intermittently kicks out of real-time and requires complete restarting. This mode is potentially attractive since it might allow concurrent operations while data is being collected. However the system does operate in single user or dedicated mode with some difficulty. Each day the system is initialized it will usually fail at least once. After that period the system usually operates normally. Several runs were lost because of system failure at the start of a run. Normally this failure can be anticipated and prevented by starting several mock runs before the data run, making a number of scans until the system fails or runs. When it runs consistently the system is deemed ready for real data collection, although failures may still occur.

Another limitation that has been noted is the fact that the system, as currently configured, is arbitrarily limited to 512 data scans. This is adequate to cover bag 1 and bag 2 of the FTP at a rate of one scan every 3 s. Each data scan is actually the average of two spectral scans but represents only one data point. Bag 1 and 2 require 1371/3 = 457 scans at a minimum, leaving 55 scans (2.75 min.) available for the start and end of the run. The data collection must be stopped, the data stored, and the system restarted between bags 2 and 3. This limitation is only a minor inconvenience for normal work but prevents the

utilization of the system on driving cycles that are longer than 1,536 s, or 25.6 min. It also prevents the collection of the total FTP in a single data set as was done with the CVS bench system.

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APPENDIX A

Detailed specifications of the desired system are as follows:

A complete FTIR analytical system for the analysis of transient automotive emissions for all regulated and a wide variety of unregulated species. The unregulated species must include formaldehyde and methanol. They should also include 1,3 butadiene, benzene, N2O, methane, the xylenes, toluene, acetylene, NO2, NO, SO2, HCN, formic acid, nitrous acid, ammonia, and the ability to accept additional compounds for analysis readily. The number of such compounds should be able to be expanded to over fifty.

This system shall include all hardware and software required to sample the exhaust emissions, analyse the composition, and present the results in a predetermined format preferably within fifteen minutes, and no more then forty five minutes, of the completion of the test. These formats will include; concentration (ppm, percent), mass (grams), mass/distance (grams/mile or kilometer) on a second by second basis and averaged or otherwise mathematically combined (at the users specification) over longer increments of time, up to the whole cycle. Such cycles will be up to one hour in length. This requires that adequate resolution be provided to allow a full analytical scan per second with appropriate averaging required for precision and the required limits of detection. This typically requires a scan resolution of 0.25 cm-1. Greater resolution should also be available, but an increase is allowed in the time between spectra. The increase in resolution should be by a factor of at least two for a three second scan and higher for longer. Better resolution is considered a positive benefit for any system.

The system should also be able to accept external input signals to allow the incorporation of other pertinent vehicle data along with the chemical composition for post run time dependent analysis. This analysis should be able to be made internally or externally by allowing data to be transferred to external computers in formats compatible with our available software. The external system most likely to be used is the IBM-AT computer system with one of several available software systems. These include Lotus 1,2,3 and dBase III+. A statistical program RS-1 is also available which uses Lotus format but does not have the capacity limitations of Lotus. The system shall have adequate capacity to internally store the interferograms from at least one run dynamically. Provision for mass storage shall be provided to allow the storage of the raw interferograms (to allow the future analysis of compounds not sought in the original analysis) and the the final data for at least one hundred runs. This storage should allow for data back up as well as primary storage with easy access to the primary analyticalsoftware. It is felt that one hundred runs should be enough to include most normal research programs but is minimal. Larger storage capacity is highly beneficial and should be as large as reasonably possible.

The internal software shall be reasonably open to allow changes to be made. This is important in the ability to add spectra, or components to be analysed, and to be able to add or change the specific algorithms used to present the data for output or further interpretation.

The sampling system shall be complete for use as a stand alone system on the direct (raw) vehicle emissions or as connected to a standard CVS system. These two configurations may be different. Both systems should provide all required information to allow the calculation of mass emission rates.

The limit of detection obtainable obviously is dependent upon the spectral characteristics of the specific compound sought. It will also be dependent upon the physical characteristics of the sample cell. The light path shall be long enough to allow the limits of detection of most components to be in the range of 0.02 ppm, when the system is run to produce a data point each second. Better signal to noise ratios allowing a lower limit of detection than specified above should be readily obtainable through the coadding of interferograms. This coadding may require more time per output (longer than one second sampling and scanning time) and software system should be capable of handling a large number of interferograms to assure optimum signal to noise ratio.

APPENDIX B

SUMMARY OF INSTRUMENT LOG

DATE MMDDYY	SIGNAL INTENS	BENCH BEAR	DETECTOR		CRASH	Misc Comments
41488			Y			Deb,Don installed system, orginal detector replaced
42588						excessive H2O, installed new vac gauge
42688						excessive H2O, leak in vac gauge
42788	9000	Y	Y	Y G	RT	Scott
42888	9000					
42988	9000					
50488		Y		Y G		Scott fixed leaky gasket
50588						leak in vac gauge, transfer error
50688						transfer error
51088					RT	2nd RT run
51188	27000		Y			installed new DBMM, Jake, Deb
51388	19000					
51688					RT	scan #39
51788					RT	scan #39, 2nd try of RT
51888					RT	scan #14, not able to do multi RT runs
53188		Y	Y			Scott, new bearings
62088	22000					
62388	27000	Y		Y G		Scott
71188	21000					would not take RT
71888	5000					cell windows dirty
71988						cell windows uncleanable
72088	6500					installed new windows(used), cleaned inside cell,mirrors
72188	26000	Y		Y G		after aligned bench-12000, then adjusted detector, Scott
72688	21000					
72788	19000					
80188	12000					
80288	12000					would not take RT
80388	11000					
80488	12000					
80588	29000	Y		Y G B		Scott
80888	32000					
81088	32000					
81188					RT	after #60
81288						gas divider busted for cal gases
81688	32000				RT	dumped core, #60
81788	32000					would not take RT
81888	32000					would not take RT
82288	32000					would not take RT
82488	32000					would not take RT
90188	12000					
90288	10000					
90688			Y			detector taken to be repaired, Scott
92788						installed new cell windows, window gasket

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 92888                      Deb, new RT software, Unix update, new
                detector
 92988 30000                Deb, new RT software, Unix update (cont)
100388 24500                moving mirror sticks
100588 19000  Y  Y          installed new bearings, Scott
100688 30000
100788 30000
101188 30600     Y          Scott, new bearings
101288 30600
101388 29000
101788 26000
101888 25000
101988 24000
102488 24000
102588 23000
102688 23000             RT #180 lost bag1+2
102788 21600             RT transfer error
110188 18000
110288 18000             RT lost bag 1+2
110388 26000                ? FTIR results low
110488 22000                ? FTIR results low
110788                      new sample line filter, tightened windows
111188                      new pressure meter and transducer
111488                      reconfigured sample line plumbing and sample
                  valves
111588 25000  Y  Y          Scott
111688 24000
111788 22000
112188 27500        Y       Scott
112288 22000     Y          no response to iris, Scott
112388 29400
112888 30200
112988 29000             RT new cmatt would not work
113088 28000
120188                      adjusted band switches for new cmatt
120288 32000
120588 32000             RT in init 1!
120688 32000                new cmatt would not work-back to old cmatt
120788 25000                init 1 locked up
121288 28000  Y  Y          init 1 locked up, slammed, Steve,loose A/D
                            connector
121388 29600             initlocked up in initl
121488 29000
 10689 26000
 10989 25000             RT in initl
 11089 25600             RT in init 1
 11189 25600
 11289 24500             RT initl
 11789 22000             initl
 11889 21800             initl
 12589  1600                slammed
 12689 21500             initl
 12789 31300  Y       Y      Dan
 20189 29300                noisy
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20289 27500              RT noisy
20689 27000                 installed new cmatt
20789 26500
20989 25400
21089 25400             initl
21389 32000  Y              new sample filter, cleaned cell, Dan
21489 30000              RT
21589 31000             initl
```

SIGNAL - SIGNAL INTENSITY IN ARBITRARY UNITS. SHOULD BE OVER 30,000
BENCH - BENCH ALIGNMENT OF MIRRORS AND OTHER OPTICAL COMPONENTS
BEAR - BEARING ADJUSTMENT OF MOVING MIRROR
DETECT - DETECTOR ADJUSTMENT
CRASH - SYSTEM FAILURE REQUIRING REBOOTING OF SYSTEM AND LOSS OF ANY COLLECTED DA

Y - ADJUSTMENT MADE
G - GAIN
B - BIAS
RT - REAL TIME MODE
INIT1 - SINGLE USER MODE
SLAMMED - MOVING MIRROR OF INTERFEROMETER NOT OPERATING PROPERLY

MATSON REPRESENTATIVES
DEB - PROGRAMMER
JAKE - SERVICEMAN
SCOTT - SERVICEMAN
DAN - SERVICEMAN
STEVE - QUALITY CONROL MANAGER

Table 1. Methanol Injections

METHANOL INJECTIONS

		INJ'D	GC	FTIR	DTN	RATIO FTIR/GC
INJ 1 NOV 28		29.6	30.5	36.8	31.4	1.207
INJ 2 NOV 28		13.9	13.3	16	13.3	1.203
INJ 3 NOV 28		64.2	58.3	72.6	61.8	1.245
INJ 4 NOV 29	PLUS EXHAUST		<QL	16.7		
INJ 5 NOV 29	PLUS EXHAUST		33	39.2		1.188
INJ 6 DEC 8	+EXHAUST	13.9	14.16	21.28		1.503
INJ 7		6.8	10.15	16.16		1.592

Table 1 Continued

DEC 8	+EXHAUST					
INJ 8 DEC 8	EXHAUST ONLY		2.85	4.15		1.456
INJ 9 DEC 8	+EXHAUST	29.6	29.03	40.70		1.402
INJ 10 DEC 8	+EXHAUST	20.3	16.77	33.89		2.021

Table 2. Formaldehyde Injections

INJECTION	INJ'D	DNPH	FTIR	RATIO DNPH/INJ	RATIO FTIR/INJ	RATIO FTIR/DNPH
1	2.22	2.4	2.36	1.081	1.063	0.983
	2.22	2.48	2.38	1.117	1.072	0.960
	2.22	2.46	2.32	1.108	1.045	0.943
			AVERAGE	1.102	1.060	0.962
			STD DEV	0.015	0.011	0.017
2	4.8	4.21	3.85	0.877	0.802	0.914
	4.8	4.81	4.34	1.002	0.904	0.902
	4.8	4.8	4.58	1.000	0.954	0.954
			AVERAGE	0.960	0.887	0.924
			STD DEV	0.058	0.063	0.022
3	10.08	6.27	5.56	0.622	0.552	0.887
	10.08	8.92	8.19	0.885	0.813	0.918
	10.08	7.81	6.6	0.775	0.655	0.845
			AVERAGE	0.761	0.673	0.885
			STD DEV	0.108	0.107	0.030
4	2.4	1.718	1.502	0.716	0.626	0.874
	2.4		1.912		0.797	
	2.4	2.318	2.912	0.966	1.213	1.256
			AVERAGE	0.841	0.879	1.045
			STD DEV	0.125	0.247	0.191
5	2.4	2.714	2.723	1.131	1.135	1.003
	2.4	2.554	2.386	1.064	0.994	0.934
	2.4	2.462	2.338	1.026	0.974	0.950
			AVERAGE	1.074	1.034	0.963
			STD DEV	0.043	0.071	0.030
6	WITH	5.27	5.68			1.078
	EXHAUST	3.78	4.57			1.209
		5.07	5.86			1.156
			AVERAGE			1.141
			STD DEV			0.054
	WHOLE		AVG	0.955	0.907	0.986
	DATA		s	0.153	0.188	0.116
	SET		NUMBER	14.000	15.000	17.000
			MAXIMUM	1.131	1.213	1.256
			MINIMUM	0.622	0.552	0.845
			RANGE			
			+ 2s	1.262	1.283	1.217
			- 2s	0.648	0.530	0.755
			REL DEV%	16.061	20.769	11.711

Table 3. Calibration Regressions

REGRESSION OF CALIBRATIONS FTIR

PROPANE
Regression Output

Constant		-0.653
Std Err of Y Est		0.700
R Squared		0.998
No. of Observations		7
Degrees of Freedom		5
X Coefficient(s)	1.165	
Std Err of Coef.	0.025	

CARBON MONOXIDE
Regression Output

Constant		17.283
Std Err of Y Est		33.286
R Squared		0.993
No. of Observations		7
Degrees of Freedom		5
X Coefficient(s)	1.038	
Std Err of Coef.	0.038	

CARBON DIOXIDE
Regression Output

Constant		0.009
Std Err of Y Est		0.037
R Squared		0.999
No. of Observations		7
Degrees of Freedom		5
X Coefficient(s)	1.085	
Std Err of Coef.	0.016	

CARBON DIOXIDE
Regression Output

Constant		-0.002
Std Err of Y Est		0.014
R Squared		1.000
No. of Observations		7
Degrees of Freedom		5
X Coefficient(s)	1.075	
Std Err of Coef.	0.005	

NITRIC OXIDE
Regression Output

Constant		6.905
Std Err of Y Est		4.746
R Squared		0.994
No. of Observations		9
Degrees of Freedom		7
X Coefficient(s)	0.794	
Std Err of Coef.	0.023	

Table 4. Carbon Dioxide Ratios

	BAG1			BAG2			BAG3		
RUN #	DTN CVS BAG	FTIR/RT	RATIO	DTN CVS BAG	FTIR/RT	RATIO	DTN CVS BAG	FTIR/RT	RATIO
30644	0.462	0.571	1.235	0.288	0.367	1.274	0.372	0.462	1.242
30645	0.456			0.288			0.372	0.406	1.091
30648	0.477	0.515	1.080	0.303	0.349	1.152	0.381	0.407	1.068
30649	0.450	0.492	1.092	0.264	0.297	1.125	0.399	0.392	0.981
30653	0.462	0.511	1.106	0.270	0.287	1.063	0.366	0.384	1.049
Average	0.461	0.522	1.128	0.283	0.325	1.154	0.378	0.410	1.086
Std. Dev.	0.009	0.029	0.062	0.014	0.034	0.077	0.012	0.027	0.086
30660	0.465	0.470	1.011	0.282	0.289	1.024	0.375	0.377	1.005
30661	0.477			0.284			0.369	0.361	0.979
30662	0.477	0.491	1.029	0.285	0.296	1.039	0.369	0.378	1.024
Average	0.473	0.481	1.020	0.284	0.293	1.032	0.371	0.372	1.003
Std. Dev.	0.006	0.010	0.009	0.001	0.004	0.007	0.003	0.008	0.018
30663	0.483			0.303			0.366	0.277	0.756
30664	0.471	0.390	0.828	0.288	0.241	0.837	0.369	0.295	0.800
30669	0.48	0.393	0.818		0.242		0.484	0.316	0.653
Average	0.478	0.391	0.823	0.296	0.242	0.837	0.406	0.296	0.736
Std. Dev.	0.005	0.001	0.005	0.008	0.001	ERR	0.055	0.016	0.061
30692	0.477	0.519	1.088	0.294	0.329	1.119	0.366	0.403	1.101
30695	0.471	0.519	1.102	0.285	0.309	1.084	0.375	0.388	1.035
30696	0.483			0.291	0.287	0.986	0.375	0.382	1.019
30697	0.468			0.282	0.297	1.053	0.381	0.378	0.992
Average	0.475	0.519	1.095	0.288	0.306	1.061	0.374	0.388	1.037
Std. Dev.	0.006	0.000	0.007	0.005	0.016	0.049	0.005	0.009	0.040
Average All	0.471	0.487	1.039	0.286	0.299	1.069	0.381	0.374	0.986
Std. Dev. All	0.010	0.054	0.122	0.010	0.036	0.104	0.029	0.045	0.142

Table 5. Carbon Monoxide Ratios

	BAG1			BAG2			BAG3		
RUN #	DTN CVS BAG	FTIR/RT	RATIO	DTN CVS BAG	FTIR/RT	RATIO	DTN CVS BAG	FTIR/RT	RATIO
30644	296.0	260.2	0.879	134.0	126.5	0.944	282.0	253.0	0.897
30645	235.0			74.0			301.0	264.5	0.879
30648	210.0	185.9	0.885	39.0	37.2	0.953	278.0	238.8	0.859
30649	207.0	196.3	0.948	128.0	126.5	0.988	256.0	229.9	0.898
30653	249.0	222.4	0.893	210.0	185.7	0.885	300.0	256.9	0.856
Average	239.4	216.2	0.901	117.0	119.0	0.942	283.4	248.6	0.878
Std. Dev.	32.3	28.7	0.027	58.3	53.1	0.037	16.5	12.6	0.018
30660	277.0	224.0	0.809	180.0	155.7	0.865	301.0	241.2	0.801
30661	265.0			103.0			293.0	232.4	0.793
30662	232.0	201.4	0.868	102.0	90.0	0.883	277.0	226.9	0.819
Average	258.0	212.7	0.838	128.3	122.9	0.874	290.3	233.5	0.805
Std. Dev.	19.0	11.3	0.030	36.5	32.8	0.009	10.0	5.9	0.011
30663	272.0			24.0			305.0	220.6	0.723
30664	245.0	186.3	0.760	107.0	84.5	0.790	301.0	219.9	0.731
30669	275.0	204.1	0.742		27.8		231.0	178.2	0.772
Average	264.0	195.2	0.751	65.5	56.1	0.790	279.0	206.2	0.742
Std. Dev.	13.5	8.9	0.009	41.5	28.4	0.000	34.0	19.8	0.021
30692	352.0	323.0	0.918	104.0	125.0	1.202	271.0	289.0	1.066
30695	292.0	265.0	0.908	95.0	98.0	1.032	311.0	282.0	0.907
30696	242.0			113.0	144.0	1.274	296.0	288.0	0.973
30697	303.0			140.0	132.8	0.949	283.0	286.0	1.011
Average	297.3	294.0	0.913	113.0	125.0	1.114	290.3	286.3	0.989
Std. Dev.	39.1	29.0	0.005	16.8	17.0	0.130	14.9	2.7	0.058
Average All	263.5	226.9	0.861	110.9	111.1	0.979	285.7	247.2	0.866
Std. Dev. All	37.0	41.6	0.065	46.9	44.3	0.138	20.5	30.3	0.095

Table 6. Nitric Oxide Ratios

	BAG1			BAG2			BAG3		
RUN #	DTN	FTIR/RT	RATIO	DTN	FTIR/RT	RATIO	DTN	FTIR/RT	RATIO
30644	12.4	13.7	1.111	4.8	5.7	1.197	11.3	13.2	1.166
30645	12.6			5.8			13.7	14.0	1.025
30648	13.8	14.4	1.040	6.0	6.4	1.068	12.8	13.5	1.059
30649		13.3			6.3		13.9	14.5	1.045
30653	14.9	15.4	1.034	6.0	6.1	1.030	13.3	13.7	1.036
Average	13.431	14.219	1.062	5.631	6.125	1.098	12.984	13.798	1.066
Std. Dev.	1.028	0.801	0.035	0.499	0.251	0.072	0.910	0.439	0.051
30660	14.4	13.447	0.934	5.0	5.091	1.021	11.9	11.629	0.979
30661	13.1			5.3			12.4	11.8	0.948
30662	13.4	12.9	0.962	5.5	5.3	0.967	12.4	11.8	0.951
Average	13.613	13.163	0.948	5.278	5.212	0.994	12.240	11.741	0.960
Std. Dev.	0.572	0.284	0.014	0.218	0.120	0.027	0.259	0.079	0.014
30663	12.9			5.1			9.9	8.2	0.830
30664		9.5			3.9			9.1	
30669	12.1	9.4	0.777	5.8	4.6	0.797	11.4	8.7	0.763
Average	12.518	9.485	0.777	5.440	4.248	0.797	10.651	8.663	0.796
Std. Dev.	0.376	0.049	0.000	0.327	0.348	0.000	0.749	0.350	0.034
30692		14.9		5.0	5.8	1.162	12.5	12.6	1.008
30695	14.4	13.2	0.917	5.2	5.2	0.990	13.7	12.6	0.920
30696	14.6			5.0	5.5	1.102	13.1	13.1	1.000
30697	14.2			5.0	4.8	0.954	13.7	12.5	0.912
Average	14.400	14.050	0.917	5.050	5.310	1.052	13.250	12.700	0.960
Std. Dev.	0.163	0.850	0.000	0.087	0.390	0.084	0.497	0.235	0.044
Average All	13.567	13.027	0.968	5.341	5.388	1.029	12.567	12.067	0.974
Std. Dev. All	0.910	1.926	0.100	0.401	0.706	0.109	1.097	1.884	0.097

Table 7. Methanol Ratios

	BAG1			BAG2			BAG3		
RUN #	GC	FTIR/RT	RATIO	GC	FTIR/RT	RATIO	GC	FTIR/RT	RATIO
30644	83.20	77.25	0.928	20.70	26.34	1.272	25.60	41.50	1.621
30645	65.30			14.00			45.80	31.07	0.678
30648	49.10	52.64	1.072	9.30	6.44	0.692	16.50	33.76	2.046
30649	46.90	50.76	1.082	12.80	14.68	1.147	21.00	32.87	1.565
30653	57.71	80.83	1.401	9.69	28.76	2.968		36.09	
Average	60.442	65.369	1.124	13.298	19.055	1.520	27.225	35.058	1.478
Std. Dev.	13.123	13.745	0.173	4.112	9.022	0.863	11.197	3.605	0.498
30660		75.300			25.000			33.600	
30661								28.089	
30662		67.911			12.530			32.859	
Average		71.606			18.765			31.516	
Std. Dev.		3.694			6.235			2.442	
30663								31.466	
30664		59.866			14.375			33.711	
30669		70.349						23.947	
Average		65.107			14.375			29.708	
Std. Dev.		5.241			0.000			4.176	
30692	66.800	89.900	1.346	11.800	18.600	1.576	28.300	37.700	1.332
30695	80.300	91.900	1.144	13.000	13.900	1.069	28.100	36.700	1.306
30696	59.890			13.250	20.400	1.540	31.920	35.300	1.106
30697	60.080			12.930			29.810	38.600	1.295
Average	66.768	90.900	1.245	12.745	17.633	1.395	29.533	37.075	1.260
Std. Dev.	8.294	1.000	0.101	0.558	2.740	0.231	1.529	1.226	0.090
Average All	63.253	71.670	1.162	13.052	18.102	1.466	28.379	33.817	1.369
Std. Dev. All	11.667	13.507	0.163	3.099	6.670	0.673	8.073	4.146	0.374

Table 8. Formaldehyde Ratios

	BAG1			BAG2			BAG3		
RUN #	DNPH	FTIR/RT	RATIO	DNPH	FTIR/RT	RATIO	DNPH	FTIR/RT	RATIO
30644	4.78	4.63	0.968	2.94	3.21	1.093	4.33	4.65	1.075
30645	4.75			2.25			3.74	4.04	1.080
30648	4.16	4.33	1.041	2.05	2.46	1.202	3.77	4.57	1.212
30649	4.28	4.57	1.068	2.45	2.70	1.101	4.23	4.56	1.077
30653	5.02	5.25	1.047	3.18	3.47	1.092	4.54	4.94	1.088
Average	4.598	4.696	1.031	2,572	2.962	1.122	4.121	4.552	1.107
Std. Dev.	0.325	0.341	0.038	0.423	0.400	0.046	0.316	0.292	0.053
30660	4.760	5.290	1.111	2.910	3.440	1.182	3.790	4.310	1.137
30661	5.270			3.780			5.070	5.827	1.149
30662	4.390	4.474	1.019	2.410	2.549	1.058	3.980	4.165	1.046
Average	4.807	4.882	1.065	3.033	2.995	1.120	4.280	4.767	1.111
Std. Dev.	0.361	0.408	0.046	0.566	0.445	0.062	0.564	0.752	0.046
30663	4.150			2.260			4.250	3.213	0.756
30664	4.32	3.275	0.758	2.58	2.050	0.795	4.09	3.256	0.796
30669		3.441			1.215			2.772	
Average	4.235	3.358	0.758	2.420	1.632	0.795	4.170	3.080	0.776
Std. Dev.	0.085	0.083	0.000	0.160	0.418	0.000	0.080	0.218	0.020
30692	8.310	7.060	0.850	2.460	2.640	1.073	4.290	3.990	0.930
30695	5.480	4.630	0.845	2.360	2.200	0.932	4.280	3.920	0.916
30696	4.830			2.500	3.060	1.224	3.900	4.120	1.056
30697	4.890			2.730	2.300	0.842	4.280	3.940	0.921
Average	5.878	5.845	0.847	2.513	2.550	1.018	4.188	3.993	0.956
Std. Dev.	1.427	1.215	0.002	0.136	0.337	0.145	0.166	0.078	0.058
Average All	4.956	4.695	0.967	2.632	2.608	1.054	4.181	4.151	1.017
Std. Dev. All	1.008	1.003	0.114	0.433	0.616	0.135	0.341	0.720	0.129

Table 9. Point by Point Comparison of Regulated Emissions

RUN # 30728	RATIOS FTIR/DTN CO2	NO	NI CO	RUN # 30735	RATIOS FTIR/DTN CO2	NO	NI CO
MAXIMUM	2.645	10.500	3.875	MAXIMUM	2.594	6.444	23.800
MINIMUM	-0.603	-4.125	-0.500	MINIMUM	-0.075	-0.313	-12.000
AVERAGE	0.971	0.546	0.897	AVERAGE	0.919	0.784	0.675
NUMBER	461	460	461	SUM BAG1	149.184	140.008	188.905
AVG BAG 1	0.932	0.884	1.021	SUM BAG2	274.528	221.590	114.888
AVG BAG 2	0.993	0.352	0.826	STD DEV	0.289	0.550	2.846
				NUMBER	461	461	450
MAXIMUM	1.496	4.592	4.056	AVG BAG1	0.888	0.833	1.145
MINIMUM	0.213	-1.267	-0.375	STD DEV	0.246	0.486	3.129
AVERAGE	0.967	0.685	0.840	AVG BAG2	0.937	0.756	0.403
SUM BAG 3				STD DEV	0.310	0.582	2.631
STD DEV	0.180	0.818	0.562				
30731				MAXIMUM	1.501	2.229	14.400
MAXIMUM	2.176	21.800	4.438	MINIMUM	0.000	-0.250	-9.600
MINIMUM	-0.511	-12.300	-0.500	AVERAGE	0.902	0.822	1.000
AVERAGE	0.988	0.542	0.975	SUM BAG 3	149.223	135.127	166.037
SUM BAG1	163.739	170.182	189.564	STD DEV	0.231	0.365	2.027
SUM BAG2	288.828	66.484	256.864	NUMBER	167	165	165
NUMBER	458	437	458				
STD DEV	0.228	2.571	0.689				
AVG BAG 1	0.963	1.044	1.115				
AVG BAG 2	1.003	0.243	0.892				
MAXIMUM	1.425	18.000	3.389				
MINIMUM	0.556	-3.500	-0.333				
AVERAGE	0.988	0.893	0.951				
SUM BAG 3	165.023	145.619	159.731				
STD DEV	0.145	2.335	0.492				
30734							
MAXIMUM	3.904	10.071	14.700				
MINIMUM	-0.438	-0.429	-3.400				
AVERAGE	1.038	0.839	0.205				
SUM BAG1	169.292	166.213	120.918				
SUM BAG2	478.656	386.556	94.415				
NUMBER	461	461	461				
STD DEV	0.454	0.863	1.269				
AVG BAG 1	1.002	0.984	0.715				
AVG BAG 2	1.059	0.755	-0.091				
STD BAG1	0.391	0.984	1.765				
STD BAG2	0.485	0.773	0.707				
MAXIMUM	1.723	2.589	3.542				
MINIMUM	0.194	-0.222	-1.020				
AVERAGE	1.010	0.798	0.315				
SUM BAG 3	166.581	131.600	51.426				
STD DEV	0.209	0.395	0.658				
NUMBER	165	165	163				

Table 10. Detailed Hydrocarbons Ratios

		FTIR	GC	RATIO
METHANE	30692	3.61	6.013	0.600
	30695	3.485	2.968	1.174
	30696	3.17	2.859	1.109
	30697	3.27	3.066	1.067
	AVG	3.384	3.727	0.987
	STD	0.173	1.322	0.227
ETHANE	30692	0.547	0.269	2.033
	30695	0.661	0.224	2.951
	30696	0.444	0.246	1.805
	30697	0.515	0.21	2.452
	AVG	0.542	0.237	2.310
	STD	0.078	0.022	0.437
ETHYLENE	30692	2.478	2.302	1.076
	30695	2.802	2.3	1.218
	30696	2.771	2.32	1.194
	30697	2.572	2.267	1.135
	AVG	2.656	2.297	1.156
	STD	0.135	0.019	0.055
ACETYLENE	30692	0.524	0.685	0.765
	30695	0.085	0.588	0.145
	30696	0.633	0.691	0.916
	30697	0.838	1.491	0.562
	AVG	0.520	0.864	0.597
	STD	0.275	0.364	0.290
PROPYLENE	30692	1.57	1.287	1.220
	30695	1.132	1.268	0.893
	30696	1.138	1.271	0.895
	30697	1.713	1.184	1.447
	AVG	1.388	1.253	1.114
	STD	0.258	0.040	0.234
1,3,BUTADIENE		0.153	0.014	10.929
	30695	0.188	0.052	3.615
	30696	0.135	0.101	1.337
	30697	0.208	0.034	6.118
	AVG	0.171	0.050	5.500
	STD	0.029	0.032	3.561

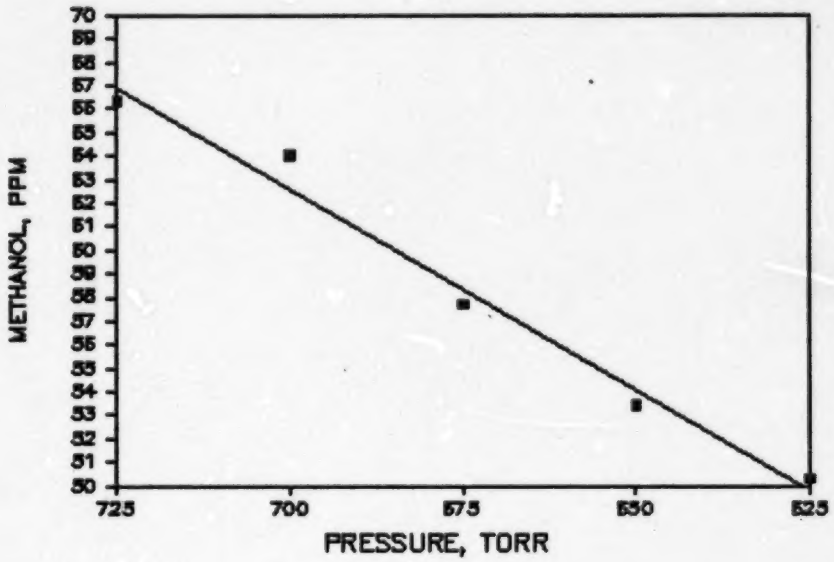
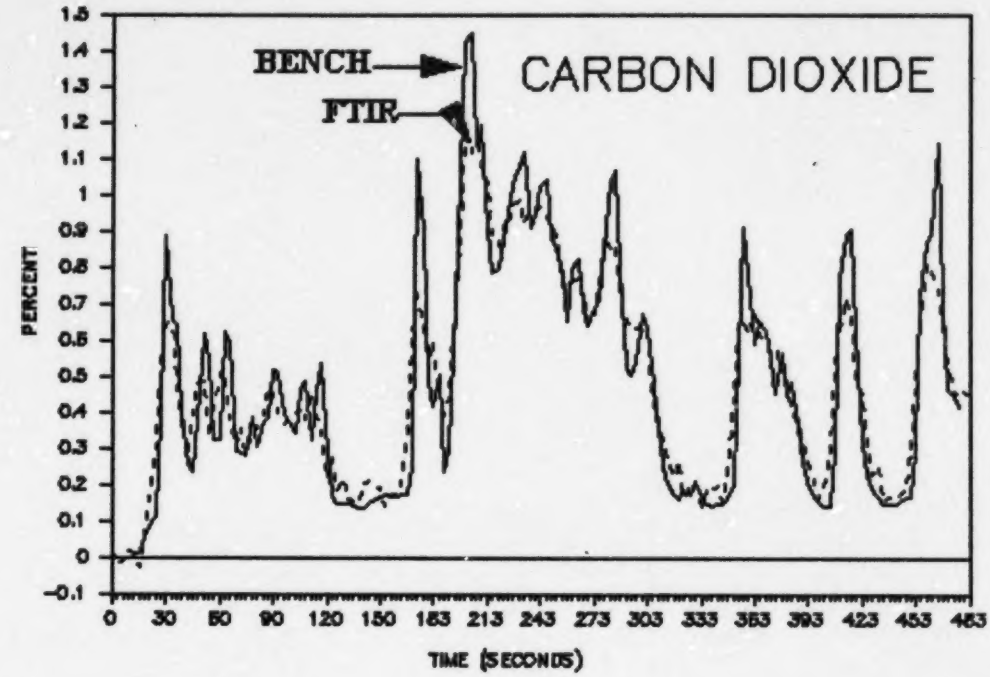


Figure 1. Concentration vs Sample Cell Pressure.



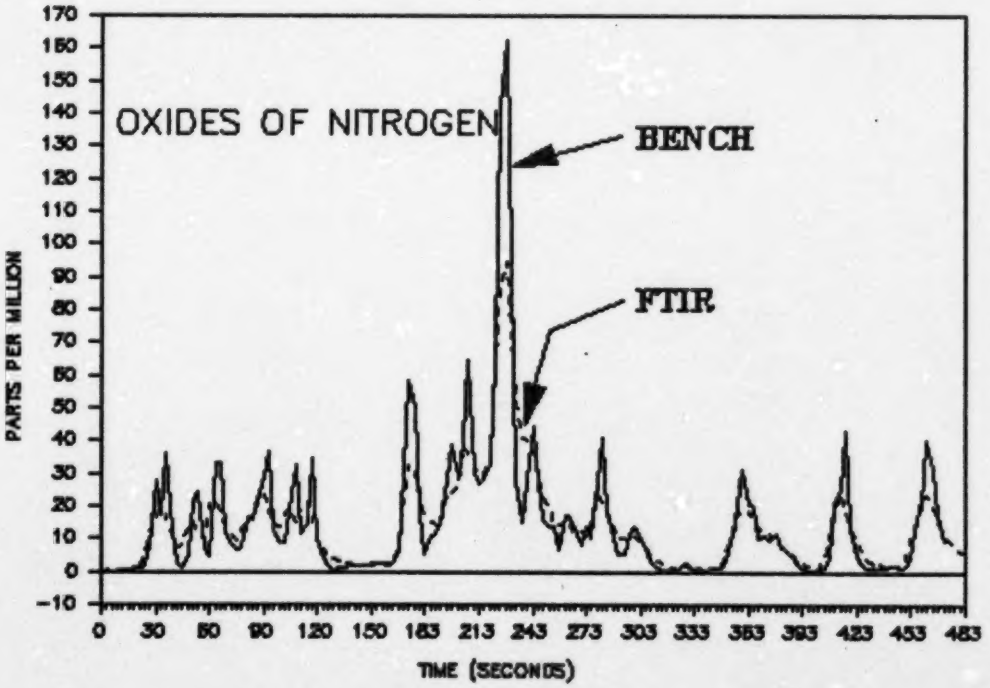


Figure 2. FTIR vs Real Time - Carbon dioxide, oxides of nitrogen.

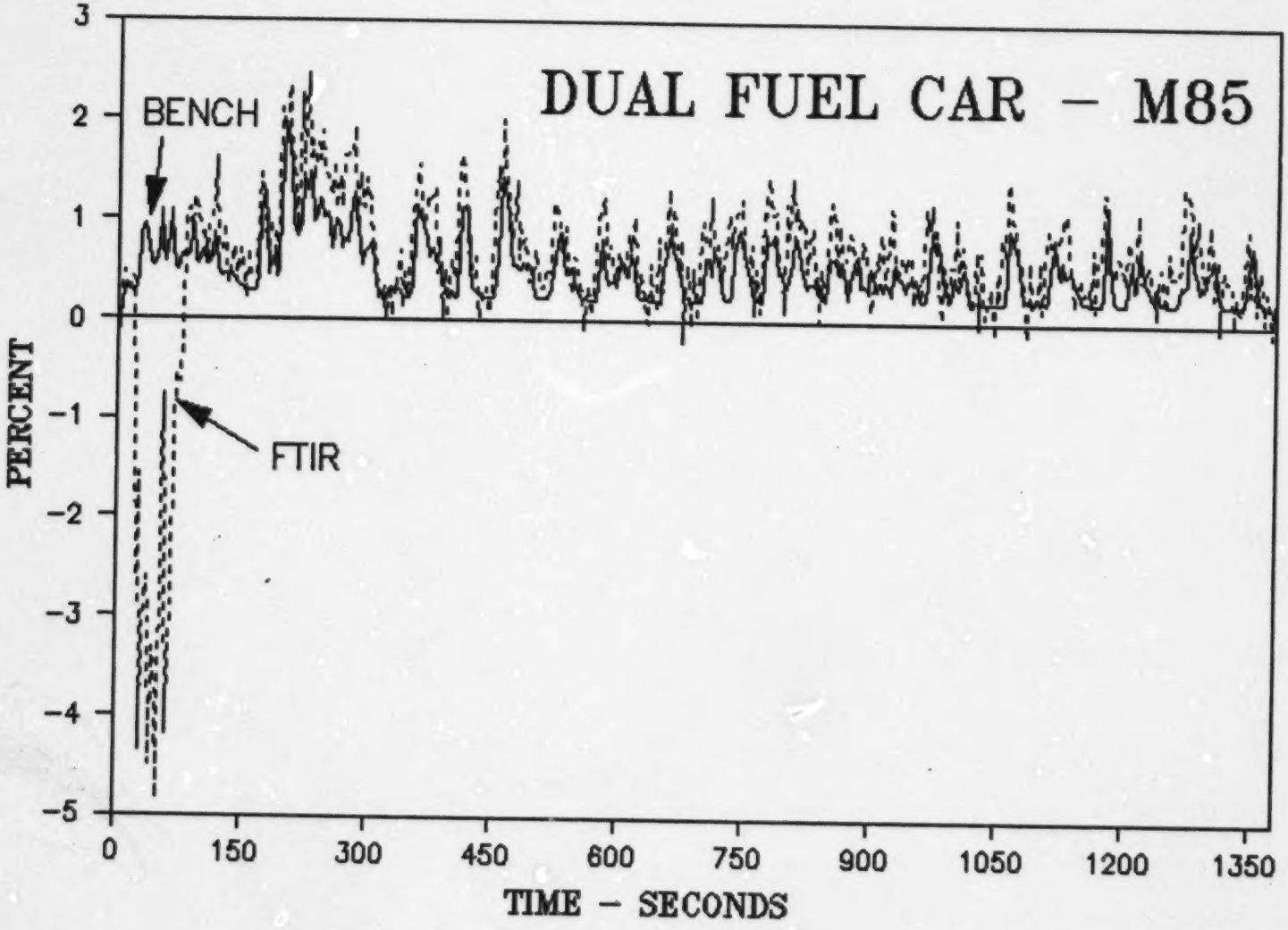


Figure 3. Carbon Dioxide - Bags 1 & 2.

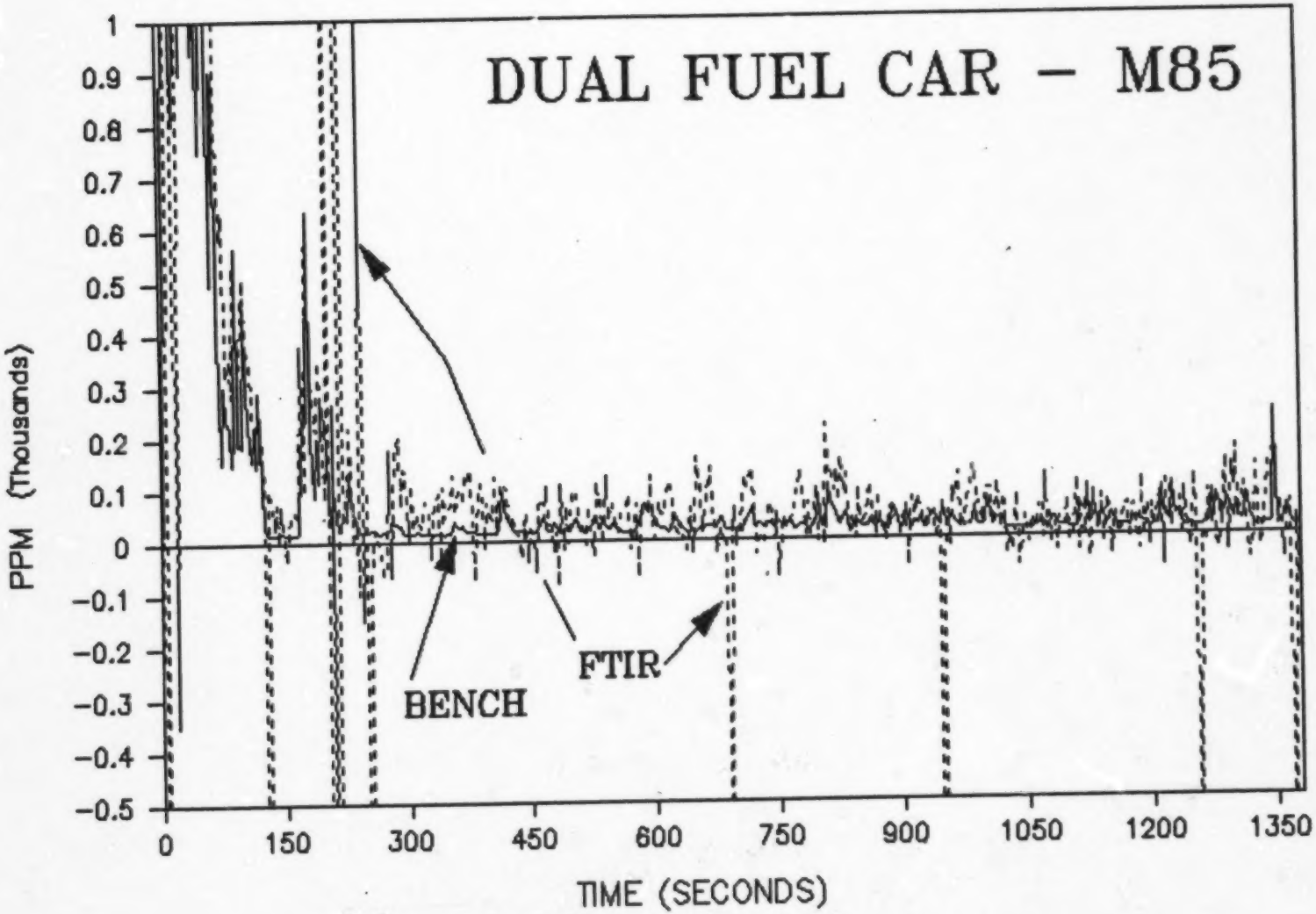


Figure 4. Carbon Monoxide - Bags 1 & 2.

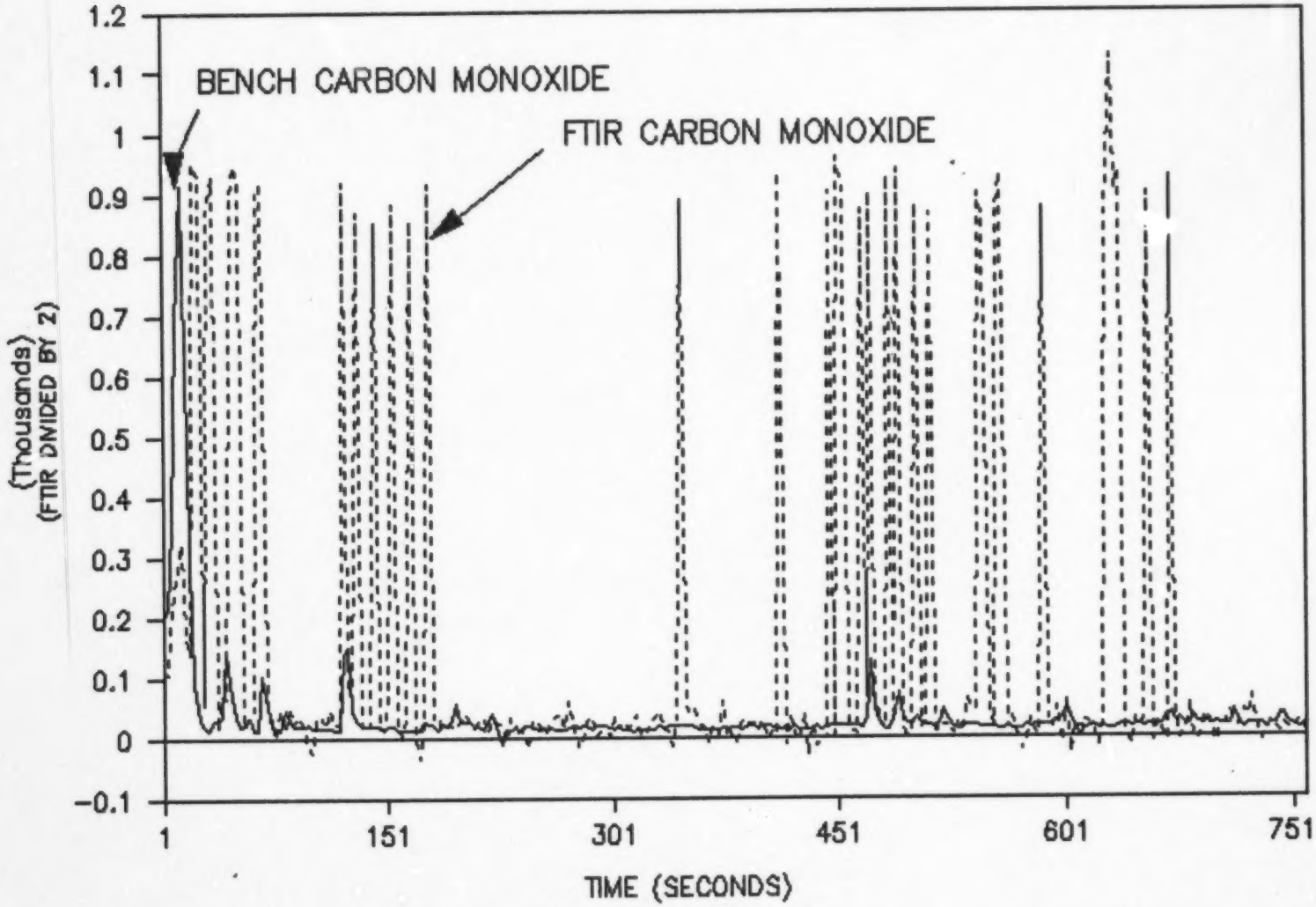


Figure 5. HWFET - Carbon Monoxide .

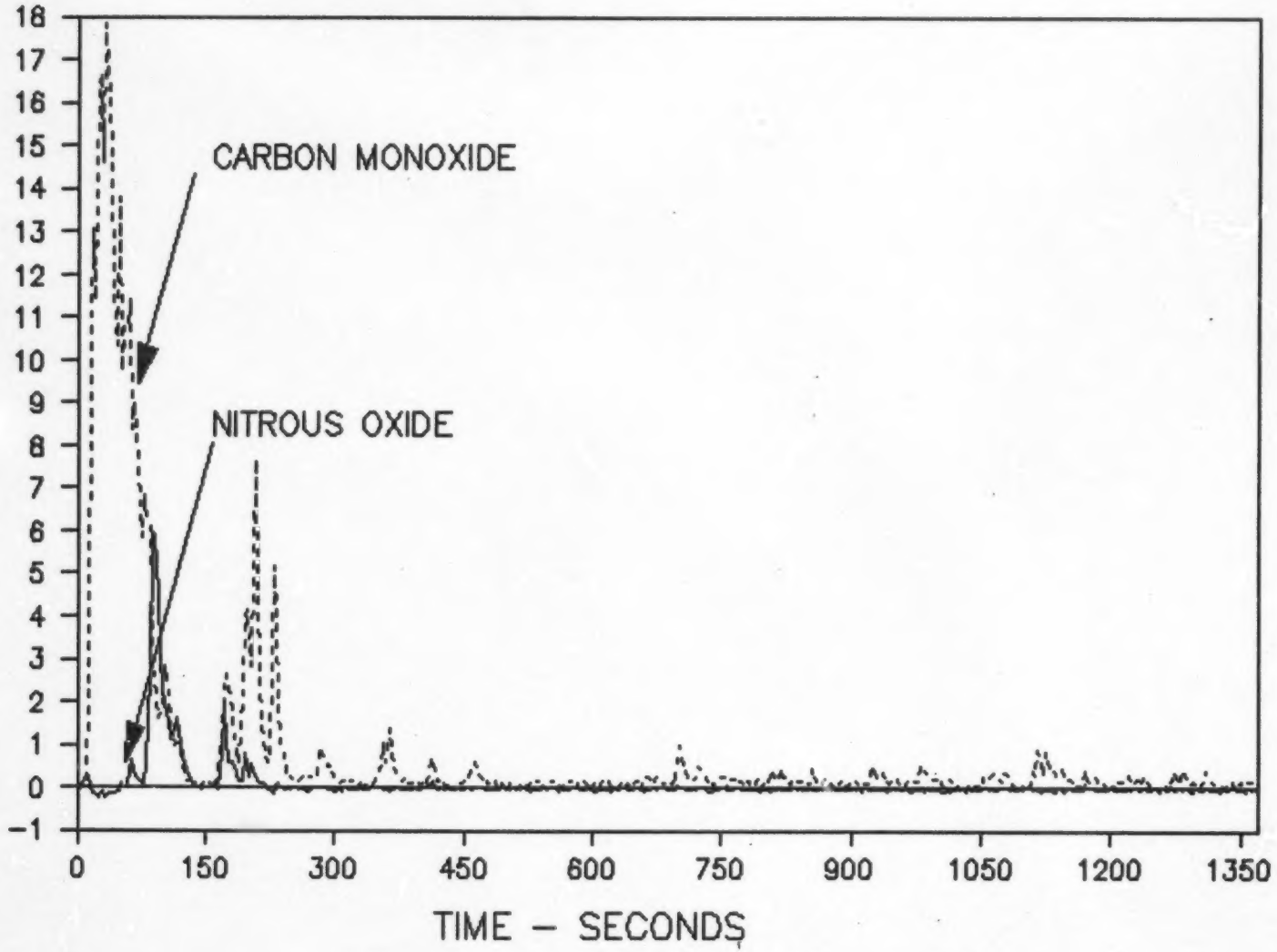


Figure 6. Emission rates versus time - CO, N_2O.

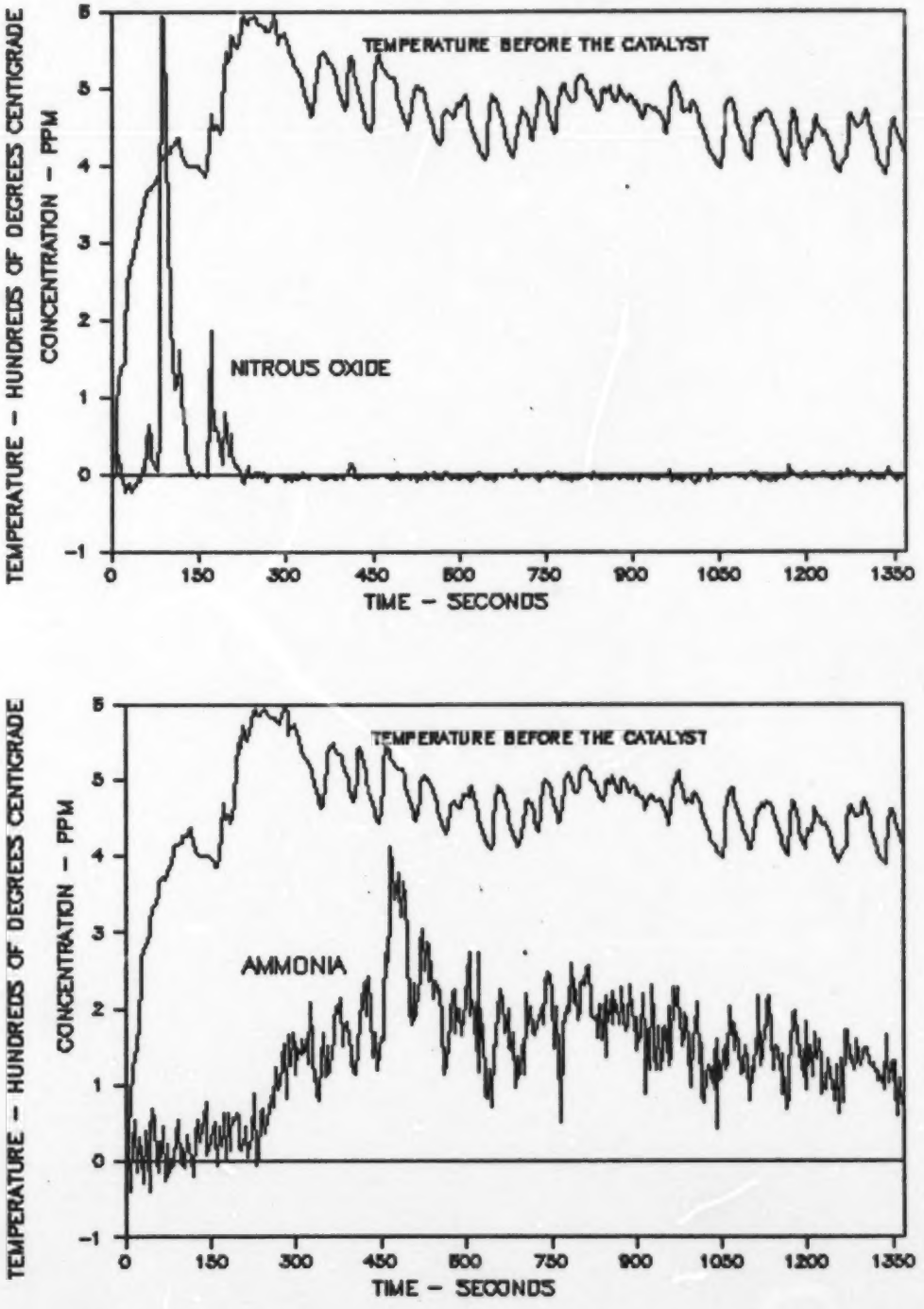


Figure 7. Emissions versus temperature - nitrous oxide, ammonia.

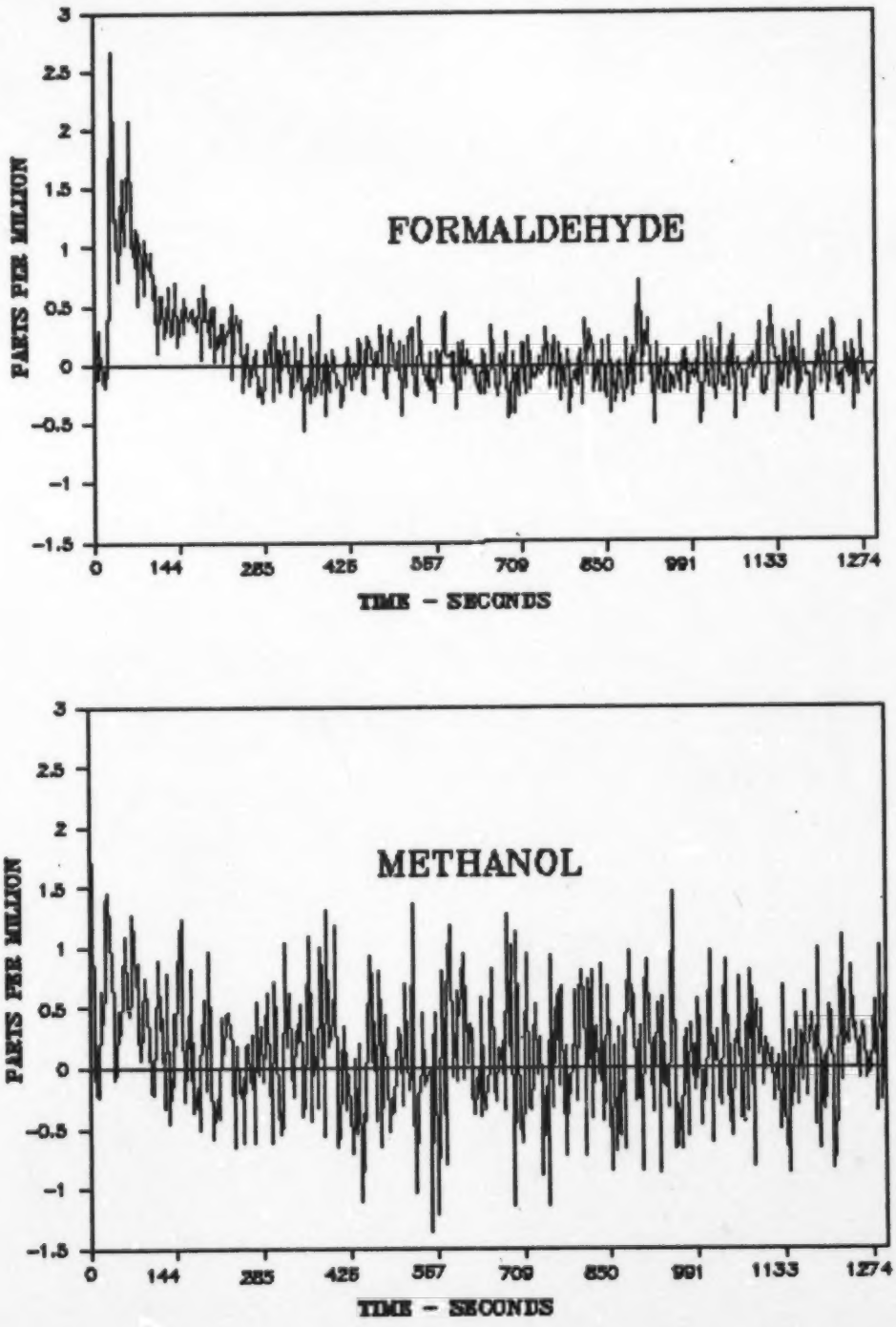


Figure 8. Real time analysis - formaldehyde, methanol.